Bull. Mater. Sci., Vol. 36, No. 7, December 2013, pp. 1191–1194. © Indian Academy of Sciences.

Luminescence properties of YAG:Nd^{3+} nano-sized ceramic powders via co-microemulsion and microwave heating

HE JUN[1,2], PANG QI[1,*], LI XIA[3] and LIANG CHUN JIE[2]

[1]College of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China
[2]Chemistry and Material College, Yulin Normal University, Yulin 537000, China
[3]Yulin Entry-xit Inspection and Qurantine Bureau, Yulin, China

MS received 13 July 2012

Abstract. Nano-sized ceramic powders with weaker aggregation of Nd^{3+}-doped yttrium aluminum garnet (YAG:Nd^{3+}) were synthesized via co-microemulsion and microwave heating. This method provides a limited small space in a micelle for the formation of nano-sized precursors. It also requires a very short heating time, thus reducing energy consumption in comparison with conventional solid-state sintering processes. As a result, small-sized particles with narrow size distribution, weaker aggregation and high purity were obtained. Powder X-ray diffraction results revealed that the structure of pure YAG:Nd^{3+} nanoparticles was cubic garnet. Transmission electron microscopy results indicated that the synthesized particles were almost spherical with average diameters of 40 and 80 nm. The luminescent properties of YAG:Nd^{3+} were investigated through PL. Under excitation at 488 nm, YAG:Nd^{3+} nano-sized ceramic powders showed main emission bands of 1045–1080 nm because of $^4F_{3/2} \rightarrow 4I_{11/2}$ transitions that are identical to those observed for a single YAG:Nd^{3+} crystal.

Keywords. Yttrium aluminum garnet; microemulsion-microwave heating; nano-sized ceramic powders; luminescence.

1. Introduction

YAG:Nd^{3+} single crystals fabricated using Czochralski method have been proven to be outstanding solid-state lasers (Sekino and Sogabe 1993). However, the fabrication of YAG single crystals using Czochralski method requires expensive equipment and crucible material and fabricating large sizes and high neodymium concentrations are difficult. Recent investigations have indicated that YAG:Nd^{3+} polycrystalline nano-sized ceramic powders are among the most promising materials for solid-state lasers (Skita *et al* 1991; Ikesue *et al* 1995; Lu *et al* 2000a, b, 2002; Hreniak and Strek 2002; Pradhan *et al* 2004; Caponetti *et al* 2007; Strek *et al* 2007; Hreniak *et al* 2008; Rabinovitch *et al* 2008). YAG powder was synthesized via different soft, low-temperature chemical routes, such as co-precipitation (Li *et al* 2004; Zhang et al 2010, 2011) and sol–gel techniques (Vaqueiro and Lopequea 1997; Veith and Mathur 1999; Wang *et al* 2006; Katelnikovas *et al* 2007). Wang *et al* (2006) reported synthesis of YAG from an EDTA acid precursor. The single polycrystalline YAG phase compounds were produced at 950 °C. Katelnikovas *et al* (2007) reported the synthesis of YAG via an EDTA sol–gel route. However, the obtained YAG were either strongly aggregated or with particle size >50 nm. An alternative approach for the production of transparent ceramics may be based on a concept of nano-sized ceramics, with the grain measuring <100 nm. In principle, ceramics with low residual porosity should be highly transparent because of the restricted Rayleigh scattering (Braun and Pilon 2006). Water-in-oil microemulsions have been used to synthesize a wide variety of nano-sized powders, such as metals, sulfides and other kinds of materials, because of the limited size of nano-sized ceramic powders (Pillai *et al* 1992; Capek 2004). Many investigations suggest that heating treatment is an important factor that controls the size and crystalline structure of products. Therefore, new methods to produce nano-sized ceramic powders and control their size and morphology must be found.

Since 1986, microwave irradiation as a heating method has found several applications in chemistry. In recent years, the use of microwave irradiation for the preparation of nano-crystalline particles has been reported (Panneerselvam *et al* 2001; Vaidhyanathan and Binner 2003). Compared with conventional methods, microwave irradiation synthesis has advantages of short reaction time, production of small particles with narrow size distribution and high purity. Using our previous work as a foundation (Pang *et al* 2003, 2007), present study reports on the preparation of YAG:Nd^{3+} nano-sized ceramic powders via co-microemulsion and microwave heating. X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS) and photoluminescence (PL) measurements were used to characterize the synthesized YAG:Nd^{3+} powders, including phase, size, morphology and luminescent properties. PL dependence of YAG:Nd^{3+} nano-sized powders on doped Nd^{3+} concentration is also presented.

*Author for correspondence (pqigx@163.com)

2. Experimental

2.1 *Preparation of YAG:Nd^{3+} nano-sized powders*

All reagents were of analytical grade. A 0·4 mol/L aqueous nitrate solution of $Y^{3+}$and Nd^{3+} (the molar ratios of $Nd^{3+}/(Y^{3+}+Nd^{3+})$ varied from 0·5 to 7%) was freshly prepared by dissolving Y_2O_3 and Nd_2O_3 in dilute nitric acid. A 1·2 mol/L $Al(NO_3)_3$ solution was obtained by dissolving $Al(NO_3)_3{\cdot}9H_2O$ in distilled water. Two microemulsions (I and II) with the same organic phase but different aqueous phases were prepared. The organic phase was composed of 24·4% Triton X-100, 16·7% *n*hexanol and 58·9% cyclohexane (mass ratio). The aqueous phase in microemulsion I was composed of $Al(NO_3)_3$, $Y(NO_3)_3$ and $Nd(NO_3)_3$ with a molar ratio of $(Y^{3+}+Nd^{3+})/Al^{3+}$ =3:5. The aqueous phase in microemulsion II has 3 mol/L $NH_3{\cdot}H_2O$ solution as a precipitating agent. Each microemulsion contained 10% aqueous solution. Equal amounts of the two microemulsions (50 mL) were mixed through continuous stirring at room temperature for 1 h. The prepared microemulsion remained transparent and was allowed to stand overnight. The precipitates of neodymium–yttrium–aluminum hydroxide were dried in a vacuum oven at 333 K for 4 h. The dried particles were placed in a corundum crucible inside a large uncovered tile crucible. The space between the corundum and the tile crucible was filled with powdered SiC. The tile crucible with dried particles was then placed in a domestic microwave oven (Model Ms-Z588SDTM, LG Company, Korea) under a microwave frequency of 2450 MHz. Varied heating time and microwave power output were used in different experiments.

2.2 *Characterization*

XRD (35 kV and 25 mA, CuKα = 1·5406 Å Rigaku/Dmax—IIIA, Tokyo, Japan) was used for crystal phase identification. TEM (JEM-1200EX) was used to investigate the morphology and size of the calcined particles. PL spectra were obtained using a standard set up with argon laser (λ_{ex} = 488 nm) at room temperature. The concentration of Nd^{3+} was determined from Kα lines of Nd^{3+} and Y using EDS installed in a Hitachi S-520 scanning electron microscope.

3. Results and discussion

3.1 *XRD*

Figure 1 shows XRD patterns of the precursor and the samples heat-treated in a microwave for 5, 10 and 20 min under 800 W power. The temperature observed was ~1073 K. No diffraction peaks appeared for the dry precursor sample, indicating that the powder was amorphous. After 5 min of heat treatment, YAG phase began to form three peaks at 2θ = 16·7°, 44·4° and 49·5° for hexagonal-$YAlO_3$ as the intermediate phase. When the heat treatment time was increased to

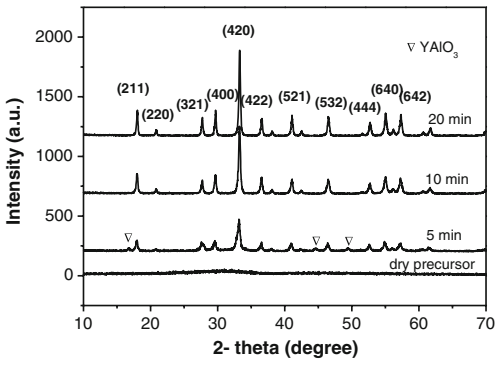

Figure 1. XRD patterns of precursor and samples heat-treated with microwave heating in 800 W for 5, 10 and 20 min, respectively.

10 min, the hexagonal-$YAlO_3$ phase peaks disappeared completely. The diffraction peaks corresponded to (211), (220), (321), (400), (420), (422), (521), (532), (444), (640) and (642) planes, which can be indexed to the pure cubic YAG phase (JCPDS-33-0040). XRD patterns of samples treated for 20 min became stronger and sharper indicating a more complete crystallization.

This result indicated that pure-phase YAG powder could be obtained using the microemulsion–microwave heating process. Through this process, the mixture of neodymium–yttrium–aluminum hydroxide precipitates were obtained in a limited small space of the aqueous droplet and were treated for a very short time with uniform heating in a microwave oven.

3.2 *TEM*

Figure 2 shows TEM micrographs of YAG:Nd^{3+} nano-sized ceramic powders heat-treated in a microwave for 10 min (a) and 20 min (b) under 800 W power. As shown in figure 2(a), most of the particles had spherical shape, weaker aggregation and a rather narrow size distribution with a diameter of ~40 nm. This result is not surprising because the nano-sized ceramic powders were synthesized by mixing the starting materials at the molecular level in a solution in a confined environment. Moreover, the nano-sized ceramic powders were heat-treated with uniform heating in a microwave oven for a very short time. As shown in figure 2(b), most of the particles had spherical shape with weaker aggregation and a diameter of 80 nm.

3.3 *Luminescence*

Figure 3 shows a typical PL emission spectrum of YAG:Nd^{3+} nano-sized ceramic powders upon 488 nm excitation at room temperature (300 K). The observed emission bands were assigned to $^4F_{3/2} \rightarrow 4I_{11/2}$ (1045–1080 nm), $^4F_{3/2} \rightarrow 4I_{11/2}$ (850–950 nm) and ($^4F_{3/2}$, $^4H_{9/2}$) $\rightarrow 4I_{11/2}$ (800–830 nm) transitions. The main emission peak is observed at ~1065 nm, which is identical to that observed

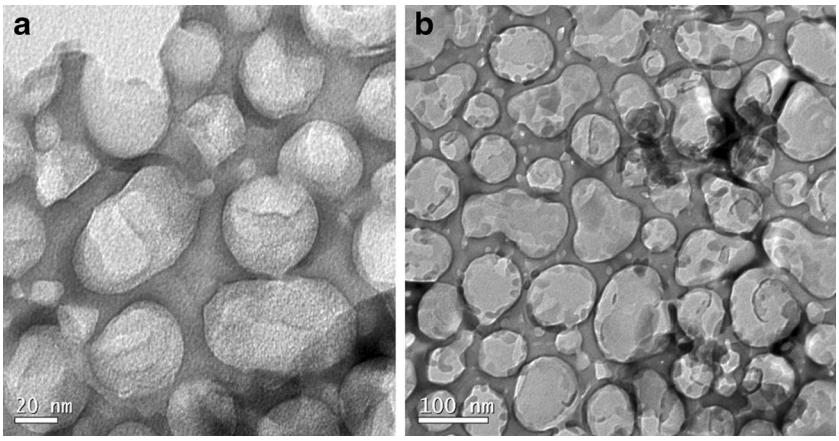

Figure 2. TEM image of YAG:Nd^{3+} heat-treated with microwave heating in 800 W for (**a**) 10 min and (**b**) 20 min, respectively.

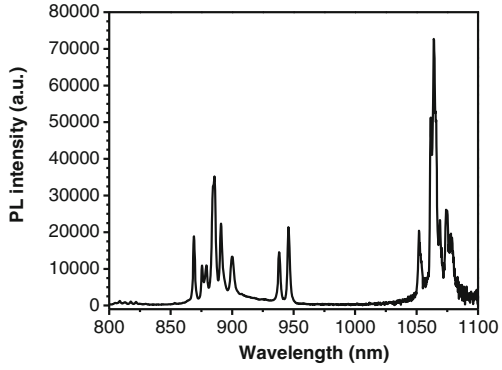

Figure 3. Photoluminescence spectrum of YAG:Nd^{3+} nano-size powder heat-treated with microwave heating in 800 W for 10 min.

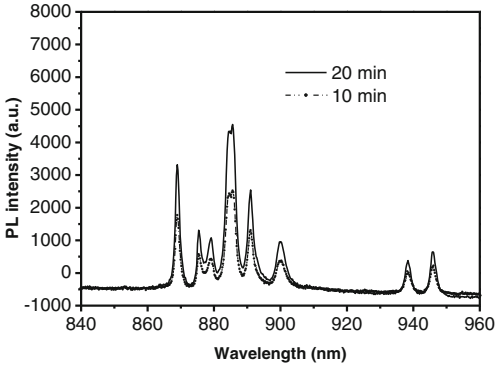

Figure 4. Photoluminescence spectrum of YAG:Nd^{3+} nano-size powder heat-treated with microwave heating in 800 W for (**a**) 10 min and (**b**) 20 min, respectively.

for a single YAG:Nd^{3+} crystal (Kshida *et al* 1968). The most significant difference of the measured luminescence spectra at room temperature is appearance of a relatively intense ($^4F_{3/2}$, $^4H_{9/2}$) $\rightarrow$ $4I_{11/2}$ transition located in the range of 800–830 nm, which was not observed in YAG:Nd^{3+} single crystal counterpart. The emission is associated with the thermalization of ($^4F_{3/2}$, $^4H_{9/2}$) terms. According to Hreniak *et al* (2007), the emission is also dependent on the sizes of YAG:Nd^{3+} nano-grain (Fedyk *et al* 2007).

Figure 4 shows that emission intensity ratio varies with the duration of heat treatment. The intensity of the sample heat-treated for 20 min is higher than that of the sample treated for 10 min because, the former has a higher degree of crystallization as confirmed by XRD results.

The effect of doped Nd^{3+} content in YAG nano-sized ceramic powders on the relative PL intensity at 1065 nm is shown in figure 5. As determined through EDS, the ratios of Nd^{3+}/(Y^{3+}+ Nd^{3+}) in the nano-sized ceramic powders were in good agreement with those of the feed. The highest PL intensity was found at a doped Nd^{3+}concentration of ~3 mol%, but further increase of Nd^{3+} doping content in the nanophosphors quench PL emission intensity. This phenomenon is attributed to concentration quenching related to interaction between an activator and sensitizer. According to Dexter and Schulman (1954), concentration quenching is in many cases due to energy transfer from one activator to another, until an energy sink in the lattice is reached. This suggests that concentration quenching is related to interaction which allows the absorbed excitation energy to reach particular quenching centers, so that the critical concentration depends on the probability of the transfer. For this reason, the critical concentration of the concentration quenching can be used as a measure of the critical distance (R_c) of energy transfer. It is possible to obtain the values of R_c from the concentration quenching data. R_c values can be practically calculated using the following equation:

$$R_c = 2\left(\frac{3V}{4\pi x_c N}\right)^{\frac{1}{3}},$$

where x_c is the critical concentration, N the number of Pr^{3+} ions in the unit cell and V the volume of the unit cell.

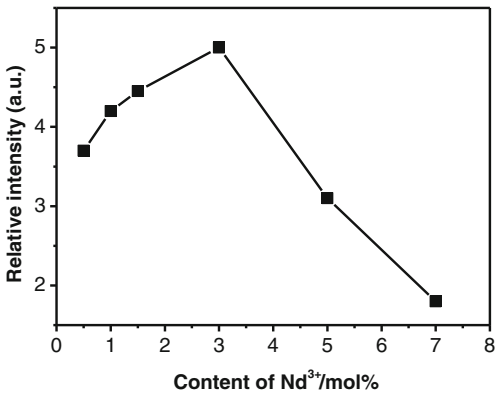

Figure 5. Effect of content of doped-Nd^{3+} on relative PL intensity at 1065 nm for YAG:Nd^{3+}nano-sized powders prepared by co-microemulsion/microwave heating (800 W, 10 min).

4. Conclusions

Pure cubic garnet of YAG:Nd^{3+} nano-sized ceramic powders with spherical shape, weaker aggregation and diameters of 40 and 80 nm were successfully prepared using a novel approach called co-microemulsion–microwave heating. This novel method is very simple and has the advantages of reactivity limited in a confined environment, short heating time, small particle size and narrow particle size distribution. Upon 488 nm excitation, YAG:Nd^{3+}nano-sized ceramic powders showed main emission bands of 1045–1080 nm because of $^4F_{3/2} \rightarrow 4I_{11/2}$ transitions that are identical to those observed for a single YAG:Nd^{3+} crystal. PL intensity increased with increasing heating time and the highest PL intensity at 1065 nm was found at a Nd^{3+}content of $\sim$3 mol%.

Acknowledgments

This research was supported by grants from the National Science Foundation of China (Grant No. 21363027) and the Natural Science Foundation of Guangxi Province (No. 2011GXNSFA018060) and the Project Sponsored by the Scientific Research Foundation of GuangXi University (Grant No. XGZ130765).

References

Braun M M and Pilon L 2006 *Thin Solid Films* **496** 505
Capek I 2004 *Adv. Colloid Interf. Sci.* **110** 49
Caponetti E, Martino D C, Saladino M L and Leonelli C 2007 *Langmuir* **23** 3947
Dexter D L and Schulman J A 1954 *J. Chem. Phys.* **V22(N6)** 1063
Fedyk R, Hreniak D, Łojkowski W, Stręk W, Matysiak H, Grzanka E, Gierlotka S and Mazur P 2007 *Opt. Mater.* **29** 1252
Hreniak D and Strek W 2002 *J. Alloy Compd* **341** 183
Hreniak D, Fedyk R, Bednarkiewicz A, Stręk W and Łojkowski W 2007 *Opt. Mater.* **29** 1244
Hreniak D, Strek W, Głuchowski P, Fedyk R and Łojkowski W 2008 *J. Alloys Compd* **451** 549
Ikesue A, Furusato I and Kamata K 1995 *J. Am. Ceram. Soc.* **78** 225
Katelnikovas A, Barkauskas J, Ivanauskas F, Beganskiene A and Kareiva A 2007 *J. Sol–Gel Sci. Technol.* **41** 193
Kshida T, Marcos H M and Geusic J E 1968 *Phys. Rev.* **167** 289
Li X, Liu H, Wang J, Cui H, Zhang X and Han F 2004 *Mater. Sci. Eng. A-Struct.* **379** 347
Lu J, Prabhu M, Xu J, Ueda K, Yagi H, Yanagitani T and Kaminskii A 2000a *Jpn J. Appl. Phys.* **39** 1048
Lu J, Prabhu M, Xu J, Ueda K, Yagi H, Yanagitani T and Kaminskii A 2000b *Appl. Phys. Lett.* **77** 3707
Lu J, Ueda K, Yagi H, Yanagitani T and Akiyama Y 2002 *J. Alloys Compd* **341** 220
Pang Q, Shi J, Liu Y, Xing D, Gong M and Xu N 2003 *Mater. Sci. Eng. B-Solid* **103** 57
Pang Q, Shi J and Gong M 2007 *J. Am. Ceram. Soc.* **90** 3943
Panneerselvam M, Subanna G N and Rao K J 2001 *J. Mater. Res.* **16** 2773
Pillai V, Kumar P and Shah D O 1992 *J. Magn. Magn. Mater.* **116** L299
Pradhan A K, Zhang K and Loutts G B 2004 *Mater. Res. Bull.* **39** 1291
Rabinovitch Y, Bogicevic C, Karolak F, Tétard D and Dammak H 2008 *J. Mater. Process Tech.* **199** 314
Sekino T and Sogabe Y 1993 *Rev. Laser Eng.* **21** 827
Skita M, Haneda H and Yanagitani T 1991 *J. Appl. Phys.* **69** 3709
Strek W, Bednarkiewicz A, Hreniak D, Mazur P and Lojkowski W 2007 *J. Lumin.* **122–123** 70
Vaidhyanathan B and Binner J G 2003 *J. Mater. Sci.* **41** 5954
Vaqueiro P and Lopequea M A 1997 *Chem. Mater.* **9** 2836
Veith M and Mathur S 1999 *J. Mater. Chem.* **9** 3069
Wang S, Xu Y, Lu P, Xu C and Cao W 2006 *Mater Sci. Eng. B-Solid* **127** 203
Zhang X L, Liu D, Sang Y H, Liu H and Wang J Y 2010 *J. Alloys Compd* **502** 206
Zhang X L, Liu D, Liu H, Wang J Y, Qin H M and Sang Y H 2011 *J. Rare Earths* **29** 585